

# Fluctuation-dissipation relation for systems with spatially varying friction

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When a particle diffuses in a medium with spatially dependent friction coefficient  $\alpha(r)$  at constant temperature  $T$ , it drifts toward the low friction end of the system even in the absence of any real physical force  $f$ . This phenomenon, which has been previously studied in the context of non-inertial Brownian dynamics, is termed “spurious drift”, although the drift is real and stems from an inertial effect taking place at the short temporal scales. Here, we study the diffusion of particles in inhomogeneous media within the framework of the inertial Langevin equation. We demonstrate that the quantity which characterizes the dynamics with non-uniform  $\alpha(r)$  is *not* the displacement of the particle  $\Delta r = r - r^0$  (where  $r^0$  is the initial position), but rather  $\Delta A(r) = A(r) - A(r^0)$ , where  $A(r)$  is the primitive function of  $\alpha(r)$ . We derive expressions relating the mean and variance of  $\Delta A$  to  $f$ ,  $T$ , and the duration of the dynamics  $\Delta t$ . For a constant friction coefficient  $\alpha(r) = \alpha$ , these expressions reduce to the well known forms of the force-drift and fluctuation-dissipation relations. We introduce a very accurate method for Langevin dynamics simulations in systems with spatially varying  $\alpha(r)$ , and use the method to validate the newly derived expressions.

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## I. INTRODUCTION

In his ground-breaking 1905 paper on Brownian motion [1], Einstein noticed that the same random thermal forces from the suspending medium that cause the diffusive motion of the particle, also produce the friction experienced by the particle when pulled through the same fluid medium. From this observation, Einstein was able to use statistical mechanics to derive the fluctuation-dissipation relation

$$D = \frac{k_B T}{\alpha}, \quad (1)$$

between the diffusion constant  $D$ , friction coefficient  $\alpha$ , temperature  $T$ , and the Boltzmann constant  $k_B$ . Three years later, Langevin introduced a very different approach to describe Brownian motion [2]. In contrast to Einstein, who considered the Fokker-Planck equation governing the particle’s probability distribution, Langevin focused on the particle’s equation of motion

$$m\dot{v} = f(r(t)) - \alpha v + \beta(t), \quad (2)$$

where  $m$  is the mass of the particle and  $v(t) = \dot{r}$  is its velocity. The Langevin equation describes Newtonian dynamics under the influences of three forces: (i) a deterministic force  $f$ , (ii) a friction force  $-\alpha v$  proportional to the velocity with friction coefficient  $\alpha \geq 0$ , and (iii) a stochastic force  $\beta(t)$  representing fluctuations arising from interactions with the embedding medium that produces the friction. The stochastic force can be conveniently modeled by a delta-correlated (“white”) Gaussian

noise with statistical properties [3]:

$$\langle \beta(t) \rangle = 0 \quad (3)$$

$$\langle \beta(t)\beta(t') \rangle = 2\alpha k_B T \delta(t - t'), \quad (4)$$

where  $\langle \dots \rangle$  means a statistical average. This statistical definition of  $\beta(t)$  ensures that the motion satisfies Einstein’s fluctuation-dissipation relation, as can be easily realized by considering the overdamped limit of Eq. (2) for a flat potential ( $f = 0$ ). In this limit, the Langevin equation simplifies to

$$\alpha v = \beta(t), \quad (5)$$

and by integrating the equation over time and using Eqs. (3) and (4), one finds that the displacement of the particle satisfies  $\langle \Delta r \rangle = 0$ , and

$$\langle (\Delta r)^2 \rangle = 2Dt, \quad (6)$$

with  $D = k_B T / \alpha$ , as in Eq. (1).

Langevin’s work began a new field in mathematics that deals with stochastic differential equations, namely equations in which one (or more) of the terms is a stochastic process. Stochastic differential equations require their own new calculus. The two most common versions of stochastic calculi were proposed and developed by Itô [4] and Stratonovich [5]. The difference between them arises in equations with multiplicative noise, e.g., in Eq. (5) with a coordinate-dependent friction coefficient  $\alpha(r)$ . In order to calculate the particle’s trajectory, one needs to integrate Eq. (5) over a time interval  $\Delta t$  [6]. For a uniform  $\alpha$ , the integral over the stochastic noise is a well-

defined Wiener process [7, 8]

$$\int_0^{\Delta t} \beta(t) dt = \sqrt{2\alpha k_B T \Delta t} \sigma, \quad (7)$$

where  $\sigma$  is a standard Gaussian random number satisfying

$$\langle \sigma \rangle = 0 \quad ; \quad \langle \sigma^2 \rangle = 1. \quad (8)$$

For a non-uniform  $\alpha(r)$ , the integral is ill-defined, since one needs to specify both the trajectory and at which points along the trajectory the friction coefficient in Eq. (7) is evaluated. In the Itô convention [4], the friction coefficient is taken at the beginning of the time interval, while the Stratonovich convention considers the algebraic mean of the initial and final frictions [5] (which, for a small time interval, can be considered close to the friction at the mid-point). Another commonly used convention is due to Hänggi [9]. The latter uses the value of the friction coefficient at the end of the time interval. In ordinary differential equations, all the above conventions result in similar trajectories when the time step becomes infinitesimal. However, the Wiener process is non-differentiable and, therefore, for the stochastic equation (5), the different calculi lead to *different* results of  $r(t)$  for arbitrarily small integration time steps (see Ref. [10], section 3.3.3). The resulting ambiguity about the appropriate way to interpret Eq. (7) is known as the Itô-Stratonovich dilemma [7, 11]. Remarkably, it is in fact the Hänggi convention that yields the correct equilibrium distribution of the particle at constant  $T$  [12], which is the reason why this interpretation is also known as the “isothermal” convention.

Diffusion in a medium with spatially dependent friction coefficient raises yet another serious problem concerning the validity of the fluctuation-dissipation theorem. Can one simply generalize Eq. (1) and write that  $D(r) = k_B T / \alpha(r)$ , and what is the physical meaning of a coordinate dependent diffusion coefficient? [13] The problem lies in the fundamental difference between friction and diffusion. The former is a quantity that can be defined locally by considering the motion of a particle in a flat potential at zero temperature. Setting  $f = 0$  and  $\beta = 0$  in Eq. (2), and integrating the equation over the time interval  $\Delta t$ , leads to

$$\begin{aligned} m\Delta v &= - \int_0^{\Delta t} \alpha(r(t)) v dt \\ &= - \int_{r^0}^{r^0 + \Delta r} \alpha(r) dr = -\alpha(r^0) \Delta r + \mathcal{O}(\Delta r)^2, \end{aligned} \quad (9)$$

where  $\Delta r = r(\Delta t) - r^0$  and  $\Delta v = v(\Delta t) - v^0$  denote the displacement and the change in velocity, respectively. Thus,  $\alpha(r^0)$  can be defined as the limiting value of  $-m\Delta v / \Delta r$ , the ratio between the change in momentum and displacement. In contrast to the friction coefficient, the diffusion constant is not a local quantity, but is rather defined by the long time asymptote of Eq. (6).

As the particle diffuses away from the point of origin, it explores new parts of the system and experiences a varying friction coefficient. For a general friction function  $\alpha(r)$ , it is not a-priori clear why the mean squared displacement should even grow linearly with  $t$ , as implied by Eq. (6). Recently, for instance, it has been argued that certain functional forms of  $\alpha(r)$  yield anomalous diffusion where  $\langle (\Delta r)^2 \rangle \sim t^z$  with  $z \neq 1$  [14]. Moreover, the problem cannot be dealt with by considering short time dynamics where the particle remains close to the initial coordinate. Eq. (6) is relevant only on time scales much larger than the relaxation time  $\tau \sim m/\alpha$ , whereas on shorter time scales the motion of the particle is ballistic and does not obey Eq. (6) at all (not even for a uniform  $\alpha$ ) [7]. These considerations suggest that the concept of spatially dependent diffusion constant is somewhat ambiguous, and that an alternative formulation for the fluctuation-dissipation relation must be sought for.

In this paper we generalize the fluctuation-dissipation relation to systems with non-uniform friction coefficients. The discussion extends our previous study on the Itô-Stratonovich dilemma, in which we focused on the “spurious drift” (see section II A below for an explanation of this term) of a particle in the presence of a friction gradient [15]. Our treatment is based on the full inertial Langevin equation (2), and we highlight the fact that the friction (dissipation) and noise (fluctuation) terms in this equation are governed by slightly different friction coefficients. We reintroduce our new “inertial” convention, which has been developed based on the analysis of Eq. (2), and which employs different friction coefficients for the fluctuation and dissipation contributions. In Ref. [15], we found both the inertial and isothermal conventions to produce the most accurate distribution functions when implemented in Langevin dynamics simulations. Here, we demonstrate that the former outperform the latter in cases when the friction coefficient changes very rapidly. We use the simulations to verify the validity of the newly derived fluctuation-dissipation relationship, as well as of other theoretical predictions.

The paper is organized as follows: In section II we derive expressions for the drift (and the associated “spurious force”) experienced by a particle when traveling in a medium with spatially dependent friction coefficient. We also present a generalized form for the fluctuation-dissipation relation. The derived expressions are tested and validated computationally in section III, where we present our method for Langevin dynamics simulations. The results are summarized and discussed in section IV.

## II. THEORY

### A. The spurious force

When a particle diffuses in a flat potential in a medium with constant  $\alpha$ , the mean displacement of the particle (averaged over an ensemble of stochastic trajectories)

ries or, equivalently, an ensemble of particles) vanishes:  $\langle \Delta r \rangle = 0$ . In the presence of a friction gradient, the mean displacement does not vanish:  $\langle \Delta r \rangle \neq 0$  - a phenomenon that has been termed “spurious drift”. The drift, which is in the opposite direction to the friction gradient, is, of course, not spurious, but rather represents the effect of inertia. It originates from the fact that when the particle travels toward a less viscous regime (i.e., against the friction gradient), it suffers less dissipation and therefore travels longer distances. This inertial effect is countered by a “trapping effect” that takes place on time scales larger than the ballistic relaxation time  $\tau \sim m/\alpha$ , and which has precisely the same origin, namely the fact that the ballistic distance decreases with  $\alpha$ . At the large time scales, the larger friction slows down the diffusion of the particle and, thus, traps it in the more viscous regime. In the case of a flat potential, the equilibrium distribution of the particle [which is independent of  $\alpha(r)$ ] is uniform, which means that, on average, the particle spends the same amount of time in each part of the system. This implies that the drift, which favors the low viscosity regime, precisely balances the slower diffusion on the high viscosity end.

Since the drift is an inertial effect, it must be dealt with within the framework of the full inertial Langevin equation (2), and not by using its strictly overdamped, non-inertial form Eq. (5). Assuming a flat potential ( $f = 0$ ), and integrating Eq. (2) over the time interval from  $t = 0$  to  $t = \Delta t$ , we arrive at the “integrated Langevin equation”

$$m\Delta v = - \int_{r^0}^{r^0+\Delta r} \alpha(r) dr + \int_0^{\Delta t} \beta(t) dt. \quad (10)$$

The terms on the r.h.s. of Eq. (10), which give the friction and noise contributions to the change in the momentum, are governed by two distinct friction coefficients representing different averages of the friction function during the time interval. The friction term features the spatially averaged friction coefficient,  $\bar{\alpha}_r$

$$\bar{\alpha}_r = \frac{\int_{r^0}^{r^0+\Delta r} \alpha(r) dr}{\Delta r} = \frac{A(r^0 + \Delta r) - A(r^0)}{\Delta r} \equiv \frac{\Delta A}{\Delta r}, \quad (11)$$

where  $A(r)$  is the primitive function of  $\alpha(r)$ . The spatially averaged friction coefficient,  $\bar{\alpha}_r$ , has the following properties: (i) It depends on the initial and final coordinates, but not on the trajectory  $r(t)$  between them. (ii) It is a well defined quantity that exists even if  $\alpha(r)$  is discontinuous. (iii) For smooth friction functions and sufficiently small  $\Delta r$ ,  $\bar{\alpha}_r$  is well approximated by the Stratonovich friction coefficient

$$\bar{\alpha}_r \simeq \frac{\alpha(r^0) + \alpha(r^0 + \Delta r)}{2} \simeq \alpha(r^0) + \frac{\alpha'(r^0)}{2} \Delta r. \quad (12)$$

The noise term in Eq. (10) is governed by a different friction coefficient. This term represents a sum of random Gaussian variables with vanishing correlation time.

Therefore, it can be *formally* written as an integral of a Wiener process [compare with Eq. (7)]

$$\int_0^{\Delta t} \beta(t) dt = \sqrt{2\bar{\alpha}_t k_B T \Delta t} \sigma, \quad (13)$$

where  $\sigma$  is a standard Gaussian random variable [see Eq. (8)], and

$$\bar{\alpha}_t = \frac{\int_0^{\Delta t} \alpha(r(t)) dt}{\Delta t} \quad (14)$$

is the time-averaged friction coefficient. In contrast to  $\bar{\alpha}_r$ , which depends only on the end points of the interval, the calculation of  $\bar{\alpha}_t$  requires full knowledge of the trajectory,  $r(t)$ , during the time step. Without this information,  $\bar{\alpha}_t$  cannot be uniquely determined since there exists not just one path, but a distribution of possible trajectories, leading from  $r^0$  to  $r^0 + \Delta r$ . This is the origin of the Itô-Stratonovich dilemma. While Eq. (14) is formally correct, it bears no physical meaning for non-zero time steps as it is based on the assumption that the noise is temporally uncorrelated (white), which is only true for vanishing  $\Delta t$ . For time steps  $\Delta t > 0$ , the friction gradient colors the noise, since the noise value at one time instance changes the trajectory of the particle and, thereby, influences the noise statistics at a following instance in time.

To address the above problem and make Eq. (10) physically unambiguous, we need to consider the ensemble average rather than a single path of the particle. On the l.h.s. of Eq. (10) we have the change in the momentum of the particle which, in the absence of deterministic forces ( $f = 0$ ), must have a vanishing ensemble average. On the r.h.s. we have the friction and noise forces. In accordance with Einstein’s idea, these terms arise from the random forces caused by the collisions with the molecules of the thermal bath. The collisions occur at such a fast rate that it can be assumed that the particle barely moves before experiencing enough collisions to make the central limit theorem applicable (see discussion in section 4.5 of Ref. [16]). Thus, the total change in the momentum of the particle during an arbitrarily small time step is normally distributed. The friction force represents the mean rate of change in the momentum, while the noise accounts for the statistical fluctuations around the mean. This implies that the ensemble average of the change in the momentum due to the noise must vanish

$$\left\langle \int_0^{\Delta t} \beta(t) dt \right\rangle = 0, \quad (15)$$

and this feature must be incorporated in the integral form of the Langevin equation (10) to make it consistent with the fluctuation-dissipation relationship. That leaves us with only the friction term in Eq. (10) whose ensemble average must therefore also vanish, and by using Eq. (11) we conclude that the drift satisfies

$$\langle \bar{\alpha}_r \Delta r \rangle = \langle \Delta A \rangle = 0. \quad (16)$$

Notice that Eq. (16) holds for any time interval  $\Delta t$  (i.e., both in the ballistic and diffusive regimes), for as long as  $f = 0$ . For a constant  $\alpha$  it reduces to the no-drift condition:  $\langle \Delta r \rangle = 0$ .

As noted above, the drift does not arise from the action of any real force but rather from the friction gradient. Using Eq. (12) in (16) we arrive at

$$\langle \Delta r \rangle \simeq -\frac{\alpha'}{2\alpha} \langle (\Delta r)^2 \rangle. \quad (17)$$

The associated spurious force is defined as the force generating a similar drift in a uniform medium. At short time scales,  $\Delta t \ll \tau \sim m/\alpha$ , the motion of the particle is ballistic ( $\Delta r \simeq v\Delta t$ ) and, thus,  $\langle (\Delta r)^2 \rangle \simeq \langle (v\Delta t)^2 \rangle = (k_B T/m)\Delta t^2$ , where the second equality is obtained by virtue of the equilibrium Maxwell-Boltzmann velocity distribution. We thus conclude that in the ballistic regime, the drift is given by

$$\langle \Delta r \rangle \simeq -\frac{1}{2} \frac{\alpha'}{\alpha} \frac{k_B T}{m} \Delta t^2, \quad (18)$$

which resembles the inertial Newtonian dynamics of a particle under the action of a (spurious) force

$$f_s = -k_B T \left( \frac{\alpha'}{\alpha} \right). \quad (19)$$

On time scales much larger than the ballistic correlation time,  $\Delta t \gg \tau$ , the motion must be compared to the diffusive dynamics of a particle in a uniform medium. For such a particle  $\langle (\Delta r)^2 \rangle = 2D\Delta t = 2(k_B T/\alpha)\Delta t$ , and by inserting this relationship into Eq. (17), we arrive at the following expression for the “spurious velocity”,  $v_s \equiv \langle \Delta r \rangle / \Delta t$

$$\alpha v_s = -k_B T \left( \frac{\alpha'}{\alpha} \right). \quad (20)$$

This result can be compared to the velocity of a particle dragged by a (spurious) force of magnitude

$$f_s = -k_B T \left( \frac{\alpha'}{\alpha} \right), \quad (21)$$

in a liquid with friction coefficient  $\alpha$ . Remarkably, Eqs. (19) and (21) provide identical expressions for the spurious force at both the short- and long-time limits, representing both ballistic and diffusive behavior.

## B. Force measurements

Part of the renewed interest in the Itô-Stratonovich dilemma stems from the relevance of the topic to experiments involving femto-Newton force measurements [17, 18]. When the particle under investigation is found close to the surface of the sample cell, its diffusion coefficients parallel and perpendicular to the boundary decrease due to the hydrodynamic interactions between the

surface and particle. In light of the debate that has erupted about the interpretation of the results of such experiments [18, 19], we here use our formalism to derive a new expression relating the displacement and the deterministic force acting on the particle. Since it is impossible to address the force variations on time scales smaller than the measurement interval  $\Delta t$ , we will assume that the force  $f$  is constant during this time frame. Without any further assumptions, we start with Eq. (10), but now in the presence of a constant deterministic force  $f$ , and we take the ensemble average of the different terms. Using Eqs. (11) and (15) we arrive at

$$m\langle \Delta v \rangle = f\Delta t - \langle \bar{\alpha}_r \Delta r \rangle = f\Delta t - \langle \Delta A \rangle. \quad (22)$$

In section II A we argued that for  $f = 0$ , there can be no change in the (ensemble) average momentum of the particle, which means that the l.h.s. of Eq. (22) must vanish for any  $\Delta t$ . This is obviously not true when  $f \neq 0$  since the force results in a change in the momentum. However, when  $\Delta t \gg \tau$ , the velocity of the particle becomes uncorrelated with the initial velocity at  $t = 0$ . Starting at  $r^0$  with an ensemble of particles with an equilibrium velocity (Maxwell-Boltzmann) distribution, the velocity distribution at  $\Delta t \gg \tau$  is expected to attain the same equilibrium form. Therefore, for  $\Delta t \gg \tau$ , the result  $\langle \Delta v \rangle = 0$  still holds, and when used in Eq. (22) it leads to

$$f = \frac{\langle \bar{\alpha}_r \Delta r \rangle}{\Delta t} = \frac{\langle \Delta A \rangle}{\Delta t}. \quad (23)$$

When the friction coefficient is constant, this expression becomes  $f = \alpha \langle v \rangle$ , where  $\langle v \rangle \equiv \langle \Delta r \rangle / \Delta t$  is the drift velocity.

When the variation in  $\alpha(r)$  during the time interval is small (yet non-negligible!), the truncated expansion on the r.h.s. of Eq. (12) can be used in Eq. (23), yielding

$$f \simeq \frac{\alpha \langle \Delta r \rangle}{\Delta t} + \frac{\alpha' \langle (\Delta r)^2 \rangle}{2\Delta t}. \quad (24)$$

If we define a spatially dependent diffusion coefficient as  $D(r) = k_B T / \alpha(r)$ , and also assume that  $\langle (\Delta r)^2 \rangle = 2D\Delta t$ , then Eq. (24) can be rewritten as

$$f \simeq \frac{\alpha \langle \Delta r \rangle}{\Delta t} - \alpha D', \quad (25)$$

where  $D' \equiv dD/dr = -k_B T (\alpha' / \alpha^2)$ . The last equation has been used in Ref. [18] for the force measurements. Unlike Eq. (23) which is asymptotically correct (for  $\Delta t \gg \tau$ ), Eq. (25) is derived with the additional assumption that  $\langle (\Delta r)^2 \rangle = 2(k_B T / \alpha)\Delta t$  which, as discussed in this paper, is an inaccurate form of the fluctuation-dissipation relation.

## C. The fluctuation-dissipation relationship

To derive the correct form of the fluctuation-dissipation relationship, we set  $f = 0$ , and start with

Eq. (10), which we now write in a slightly different form

$$m\Delta v + \bar{\alpha}_r \Delta r = \int_0^{\Delta t} \beta(t') dt'. \quad (26)$$

By squaring the equation and taking the ensemble average, we arrive at

$$\begin{aligned} & \langle (m\Delta v)^2 + 2m\Delta v \bar{\alpha}_r \Delta r + (\bar{\alpha}_r \Delta r)^2 \rangle \\ &= \int_0^{\Delta t} dt'' \int_0^{\Delta t} dt' \langle \beta(t'') \beta(t') \rangle. \end{aligned} \quad (27)$$

At large times,  $\Delta t \gg \tau$ , the expression on the l.h.s. of this equation is dominated by the third term, which roughly grows linearly with  $\Delta t$  while the other two terms remain finite. The term on the r.h.s. can be evaluated by using Eq. (4) with  $\alpha = \alpha(t)$ . This leads us to the asymptotic equation

$$\langle (\bar{\alpha}_r \Delta r)^2 \rangle = \langle (\Delta A)^2 \rangle = \int_0^{\Delta t} 2\langle \alpha(t) \rangle k_B T dt, \quad (28)$$

which is the generalized form of the fluctuation-dissipation relationship for system with spatially dependent friction. For a constant friction coefficient  $\alpha$ , the relationship reduces to the well known form  $\langle (\Delta r)^2 \rangle = 2(k_B T / \alpha) \Delta t$ . Notice that  $\langle \alpha(t) \rangle = \langle \alpha(r(t)) \rangle$  can also be expressed as

$$\langle \alpha(r(t)) \rangle = \int_0^{\Delta t} \rho(r, t) \alpha(r) dr, \quad (29)$$

where  $\rho(r, t)$  is the normalized distribution function of the particle at time  $t$ . This implies that  $\langle \alpha(r(t)) \rangle$  depends on the initial distribution  $\rho(r, 0)$ . If the particle is initially localized at  $r = r^0$ , then  $\rho(r, 0) = \delta(r - r^0)$ .

Another interesting case is that of an infinite system with average nonzero density  $\rho_0 = 1/L$ , modeled by periodic boundary conditions to a system with finite length  $L$ . If the initial distribution  $\rho(r, 0)$  coincides with the equilibrium distribution, which (for  $f = 0$ ) is uniform  $\rho(r, t) = \rho_{eq}(r) = 1/L$ , then Eq. (28) simplifies to

$$\langle (\Delta A)^2 \rangle = 2\langle \alpha \rangle k_B T \Delta t, \quad (30)$$

with  $\langle \alpha \rangle = L^{-1} \int \alpha(r) dr$ . However, the far l.h.s. of Eq. (28) *cannot* be replaced with  $\langle \alpha \rangle^2 \langle (\Delta r)^2 \rangle$  [or  $\langle \alpha^2 \rangle \langle (\Delta r)^2 \rangle$ ] in this case, since the latter form does not account correctly for the drift of the particle. This highlights the fact that  $\Delta A$ , and not  $\Delta r$ , is the quantity that characterizes the displacement of the particle when traveling in an inhomogeneous medium. This conclusion is also reflected in Eqs. (16) and (23).

#### D. Fick's second law

We conclude the analytical part of the paper by returning to our earlier comment [see text after Eq. (9)]

that the concept of a spatially dependent friction coefficient  $D(r)$  is non-trivial since diffusion is inherently a non-local process. This has motivated us, throughout section II, to derive expressions involving only the local friction coefficient  $\alpha(r)$ . The only context in which  $D(r)$  can be rationalized is the Fokker-Planck equation for the probability density of the particle  $\rho(r, t)$ , which can be derived as follows: For the simplicity of the presentation (but without limiting the generality of the derived equation), let us assume that the particle initially is located at  $r^0$  [i.e.,  $\rho(r, 0) = \delta(r - r^0)$ ]. We start by rewriting Eq. (28) [together with Eq. (29)] in the following explicit form

$$\int_{-\infty}^{\infty} dr' B^2(r') \rho(r', t) = 2k_B T \int_0^t dt' \int_{-\infty}^{\infty} dr' \alpha(r') \rho(r', t'), \quad (31)$$

where  $B(r) \equiv \Delta A(r) = A(r) - A(r^0)$ . Taking the partial derivative with respect to  $t$  gives

$$\begin{aligned} \int_{-\infty}^{\infty} dr' B^2(r') \frac{\partial \rho(r', t)}{\partial t} &= 2k_B T \int_{-\infty}^{\infty} dr' \alpha(r') \rho(r', t) \\ &= -2k_B T \int_{-\infty}^{\infty} dr' B(r') \frac{\partial \rho(r', t)}{\partial r'}, \end{aligned} \quad (32)$$

where the second equality is obtained via integration by parts, keeping in mind that  $B'(r) = \alpha(r)$  and using the fact that  $\rho(r, t)$  vanishes for  $r \rightarrow \pm\infty$ . By multiplying and dividing the integrand on the r.h.s. of Eq. (32) by  $\alpha(r')$ , and using the identity  $2B(r)\alpha(r) = 2B(r)B'(r) = [B^2(r)]'$ , we arrive at

$$\begin{aligned} \int_{-\infty}^{\infty} dr' B^2(r') \frac{\partial \rho(r', t)}{\partial t} &= \\ -k_B T \int_{-\infty}^{\infty} dr' [B^2(r')] \frac{1}{\alpha(r')} \frac{\partial \rho(r', t)}{\partial r'}. \end{aligned} \quad (33)$$

Integrating by parts the r.h.s. of Eq. (33) yields

$$\begin{aligned} \int_{-\infty}^{\infty} dr' B^2(r') \frac{\partial \rho(r', t)}{\partial t} &= \\ \int_{-\infty}^{\infty} dr' B^2(r') \frac{\partial}{\partial r'} \left[ \frac{k_B T}{\alpha(r')} \frac{\partial \rho(r', t)}{\partial r'} \right]. \end{aligned} \quad (34)$$

Since Eq. (34) holds for any function  $B(r)$  it must be that

$$\frac{\partial \rho(r, t)}{\partial t} = \frac{\partial}{\partial r} \left[ \frac{k_B T}{\alpha(r)} \frac{\partial \rho(r, t)}{\partial r} \right]. \quad (35)$$

The last equation is Fick's second law, which is commonly written as  $\partial_t \rho = \partial_r [D(r) \partial_r \rho]$ , with  $D(r)$  being the spatially dependent diffusion coefficient. Comparing this form to Eq. (35), we find that  $D(r) = k_B T / \alpha(r)$ , which is the natural generalization of Eq. (1).

### III. LANGEVIN DYNAMICS SIMULATIONS

In the previous section we demonstrated that much of the Itô-Stratonovich dilemma can be resolved by: (i) con-

sidering the inertial Langevin equation (2) rather than its overdamped, non-inertial limit (5), (ii) taking the ensemble average over many stochastic trajectories, and (iii) enforcing Eq. (15) for the contribution of the noise to the momentum of the particle. This has led to the derivation of Eqs. (16), (23), and (28), which we now test using computer simulations. When performing Langevin dynamics simulations, a set of algebraic equations (an “integrator”) is used to generate stochastic trajectories of the particle. Choosing the appropriate convention to be implemented in the integrator invokes the Itô-Stratonovich dilemma in a slightly different form, as will be discussed in the following section.

For the Langevin dynamics simulations, we use the GJF integrator [20] which, starting with  $r = r^n$  and  $v = v^n$  at  $t = t_n$ , uses the following equations for calculating the position,  $r^{n+1}$ , and velocity,  $v^{n+1}$ , at time  $t_{n+1} = t_n + dt$

$$r^{n+1} = r^n + bdtv^n + \frac{bdt^2}{2m}f^n + \frac{bdt}{2m}\sqrt{2\alpha k_B T dt}\sigma^{n+1} \quad (36)$$

$$v^{n+1} = av^n + \frac{dt}{2m}(af^n + f^{n+1}) + \frac{b}{m}\sqrt{2\alpha k_B T dt}\sigma^{n+1}, \quad (37)$$

where  $f^n = f(r^n)$ ,  $\sigma^n$  is a random Gaussian number satisfying Eq. (8), and the coefficients  $a$  and  $b$  are given by

$$b = \left(1 + \frac{\alpha dt}{2m}\right)^{-1} \quad (38)$$

$$a = b\left(1 - \frac{\alpha dt}{2m}\right). \quad (39)$$

For a constant friction coefficient  $\alpha$ , it was analytically demonstrated that the GJF integrator provides exact thermodynamic response for both flat and harmonic potentials for any time step  $dt$  within the stability criterion of the method [20]. For spatially dependent friction  $\alpha(r)$ , one needs to choose the value of  $\alpha$  to be used in Eqs. (36)-(39). The conventions of Itô, Stratonovich, and (Hänggi) (the isothermal) correspond to setting  $\alpha = \alpha(r^n)$ ,  $\alpha = [\alpha(r^n) + \alpha(r^{n+1})]/2$ , and  $\alpha = \alpha(r^{n+1})$ , respectively. None of these interpretations is physically accurate since, as our discussion in section II A reveals, the important friction coefficients are  $\bar{\alpha}_r$  (11) and  $\bar{\alpha}_t$  (14). The former governs the friction term in Eq. (10) and, therefore, is the one to be used in expressions (38) and (39) for the coefficients  $b$  and  $a$  characterizing the dissipation decay rate of the velocity. The latter should be used for the noise amplitude,  $(2k_B\bar{\alpha}_t dt)^{1/2}$ . For smooth friction functions,  $\bar{\alpha}_r$  differs by  $\mathcal{O}(dt)$  from the value used in the Itô and isothermal interpretations, and by  $\mathcal{O}(dt^2)$  from the Stratonovich value. This may indicate that the most accurate interpretation is that of Stratonovich. Unfortunately, the Stratonovich friction coefficient uses information about the position of

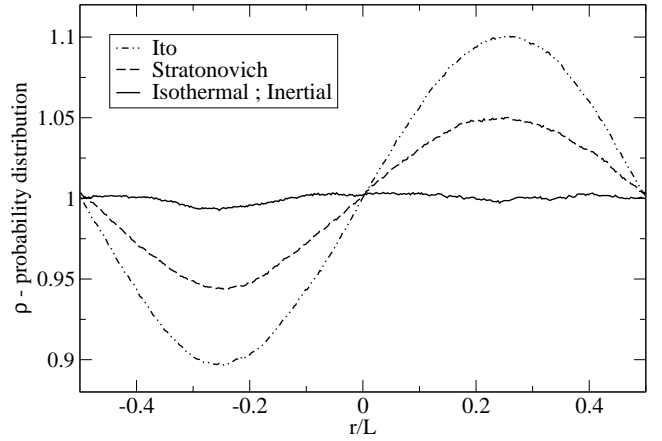


FIG. 1: The probability distribution computed using Itô (dashed-dotted), Stratonovich (dashed), isothermal (solid line), and the new inertial (same solid line - curve is indistinguishable from the isothermal curve at the resolution of the graph) interpretations. The results correspond to a particle diffusing in a flat potential with a friction function that has a sinusoidal form. The results for the different conventions were computed with the same normalized time step  $dt = 0.1$ .

the particle at the end of the time step. Therefore, using this value in Eq. (13), would result in violation of Eq. (15), which must be satisfied by the stochastic noise term. The isothermal interpretation suffers from exactly the same deficiency of the noise term, while Itô’s convention, despite satisfying Eq. (15), assumes a value which clearly deviates by  $\mathcal{O}(dt)$  from  $\bar{\alpha}_t$ .

In our previous work we proposed a new “inertial” convention [15], where  $\bar{\alpha}_r$  (11) is used for the coefficients  $a$  and  $b$ , while

$$\begin{aligned} \bar{\alpha}_t &\simeq \bar{\alpha}_r(r^n \rightarrow r^n + v^n dt) = \frac{\int_{r^n}^{r^n + v^n dt} \alpha(r) dr}{v^n dt} \\ &= \alpha(r^n) + \alpha'(r^n)\frac{v^n dt}{2} + \mathcal{O}(dt^2), \end{aligned} \quad (40)$$

is used for the noise amplitude. The fact that the friction coefficient given by Eq. (40) is based on information existing at  $t = t_n$  only, makes  $(2\bar{\alpha}_t k_B T dt)^{1/2} \sigma$  a true Gaussian variable and ensures that Eq. (15) is obeyed. Expression (40) is essentially the best guess that one can make for  $\bar{\alpha}_t$  at  $t = t_n$ . It involves the assumption that the particle travels with velocity  $v^n$  during the time step. This is a reasonable estimation of  $\bar{\alpha}_t$  for small time steps  $dt \ll \tau$ , during which the trajectory of the particle is nearly ballistic.

Obviously, neither the newly proposed inertial convention nor the above mentioned more familiar ones (Itô, Stratonovich, isothermal) are exact for discrete time steps. The fact that the integrator numerically solves the inertial Langevin equation (2) and not its non-inertial form (5), guarantees that the correct equilibrium distribution is obtained when  $dt \rightarrow 0$  for *any* sensible interpretation. The difference between the conventions, as implemented for inertial Langevin dynamics, is simply the

rate of convergence to the correct distribution for  $dt \rightarrow 0$ . This may seem as a lighter version of the Itô-Stratonovich dilemma, which is *only* a fundamental issue if the inertial term is entirely omitted in the Langevin equation. However, the rate of convergence has a considerable practical importance in simulations where the time step  $dt$  is not infinitesimal. The difference between the conventions is demonstrated in Fig. 1, showing the simulated spatial equilibrium distribution of a particle of normalized mass  $m = 1$ , in contact with a constant temperature bath  $T$ , moving in a one-dimensional medium with a flat potential and a sinusoidal normalized friction coefficient given by  $\alpha(r) = 2.75 + 2.25 \sin(2\pi r/L)$ , where  $L = 40$  is the spatial extension of the system in normalized units. All the results depicted in Fig. 1 were derived from simulations with normalized time step  $dt = 0.1$ . Since the potential energy is constant, the equilibrium distribution must be uniform. Our results show that both Itô and Stratonovich interpretations exhibit noticeable deviations from the correct uniform equilibrium distribution. The deviations reflect the sinusoidal form of the friction function. In contrast, the isothermal and inertial conventions produce indistinguishable distributions that are fairly uniform and deviate by less than 0.5% from the correct value of 1.

The ability of the isothermal and inertial conventions to accurately sample the equilibrium distribution function while using relatively large time steps was discussed in details in Ref. [15]. In short, the reason lies in the fact that these conventions account correctly for the drift of the particle, although this happens in very different ways. In the inertial convention the drift originates from the dissipation term in the integrated Langevin equation, while the noise term in that equation has zero mean, in accordance with Eq. (15). In contrast, in the isothermal convention, Eq. (15) for the noise is not satisfied, and the drift is generated by the friction term being larger than necessary. Fortunately for the isothermal convention, these two errors cancel each other. In simulations we observed that, when starting with the same initial position and velocity and using the same seed for the Gaussian random number generator, the isothermal and inertial conventions produced nearly identical trajectories, which explains why the resulting probability distributions depicted in Fig. 1 are indistinguishable.

The discussion in the previous paragraph is valid only for smooth friction functions for which the change in the friction coefficient during the time step is small. When  $\alpha(r)$  exhibits rapid spatial variations, the more physically-based inertial convention performs much better than the isothermal one. This is nicely demonstrated in Fig. 2, showing the results of simulations similar to those depicted in Fig. 1, with the only difference being that the sinusoidal friction function has been replaced with the step-function  $\alpha(r) = 0.5 + 4.5\Theta(r)$ , where  $\Theta(r)$  is the Heaviside step function. As in Fig. 1, the deviation from a uniform probability distribution depicted in Fig. 2 follows the form of the simulated friction function.

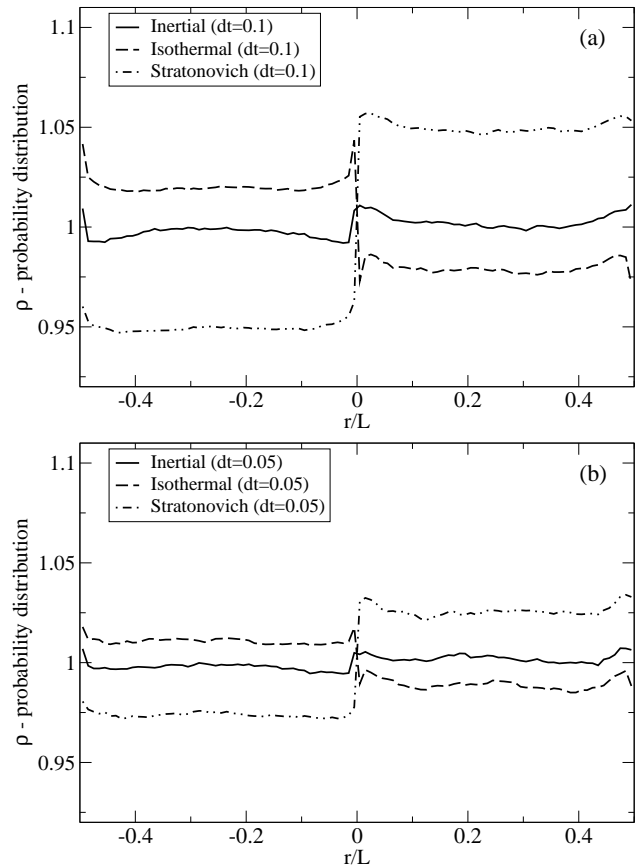


FIG. 2: Probability distribution computed using Stratonovich (dashed-dotted), isothermal (dashed), and inertial (solid line) interpretations. The results correspond to a particle diffusing in a flat potential with a step friction function. The results for the different conventions were computed with (a)  $dt = 0.1$  and (b)  $dt = 0.05$ .

In contrast to Fig. 1, the isothermal and inertial conventions do not generate similar trajectories and distribution functions. The latter, albeit not exact, is clearly superior to the former. For comparison, the results of the Stratonovich convention are also displayed. Notice (by comparing Figs. 2(a) for  $dt = 0.1$  and (b) for  $dt = 0.05$ ) the fundamental difference between the Stratonovich and isothermal results which appear as step functions with an amplitude scaling linearly with  $dt$ , and the inertial convention which, away from the discontinuity in  $\alpha$  (at  $r = 0$ ), recovers the correct value  $\rho = 1$ .

Fig. 3 shows the distribution function computed from simulations of a particle traveling in a medium with the same step friction function as in Fig. 2, but in this case within a harmonic potential well  $U = kr^2/2$  with a normalized spring constant  $k = 2$ . When the deterministic force does not vanish (as in this case), Eq. (40) can be modified to  $\bar{\alpha}_t \simeq \bar{\alpha}_r(r^n \rightarrow r^n + v^n dt + f^n dt^2/2m)$ , although the impact of the new term involving  $f^n$  is nearly negligible for small  $dt$ . Our results demonstrate, once again, the advantage of the inertial interpretation over the isothermal one in produc-

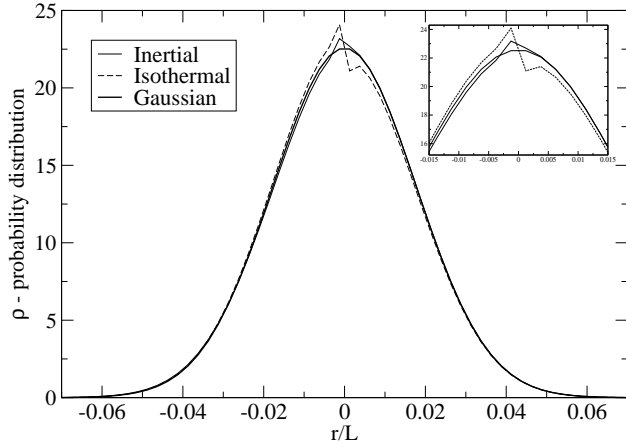


FIG. 3: Probability distribution computed using the isothermal (dashed), and inertial (solid line) interpretations. Results correspond to a particle diffusing in a harmonic potential with normalized natural frequency  $\sqrt{k/m} = \sqrt{2}$  and with a step friction function. Results for the different conventions were computed with  $dt = 0.1$ . Thick solid line depicts the exact equilibrium Gaussian distribution. Inset shows a magnification of the central region of the distribution.

ing accurate distribution with relatively large time steps ( $dt = 0.1$  in Fig. 3). Notice that both interpretations converge to the correct Gaussian form,  $\rho_{\text{eq}}(r) = (k/2\pi k_B T)^{1/2} \exp(-kr^2/2k_B T)$ , away from the interface between the two friction regimes. This observation can be traced to the fact that for a constant  $\alpha$  and a harmonic potential, the GJF integrator generates the exact Gaussian distribution [20].

Having established the GJF integrator with the inertial convention as the best available method for simulating dynamics in systems with space-dependent friction, we now wish to use this method to examine the validity of the theoretical predictions from section II. We start with the relation  $\langle \bar{\alpha}_r \Delta r \rangle = 0$  (16) governing the drift of the particle in the absence of a deterministic force ( $f = 0$ ). We consider a particle moving in a medium with the following “ramp” friction function

$$\alpha(r) = \begin{cases} 0.5 & \text{for } r < -10 \\ 0.5 + 0.225(r + 10) & \text{for } -10 \leq r \leq 10 \\ 5.0 & \text{for } r > 10 \end{cases} \quad (41)$$

Starting at  $r^0 = 0$  with a velocity randomly drawn from the equilibrium Maxwell-Boltzmann distribution, we follow the particle and record its position as a function of the time  $\Delta t$ . We set the integration time step to  $dt = 0.01$ , which is 10 times smaller than the time step used in Figs. 1–3. The ensemble average is calculated by repeating this procedure for  $10^7$  different stochastic trajectories. The results, depicted by solid circles in Fig. 4, are in full agreement with Eq. (16). For comparison, we also show (open squares) the temporal dependence of  $\alpha_0 \langle \Delta r \rangle$  (where  $\alpha_0 = \alpha(r^0) = 2.75$ ). As expected, the data reveals that there is an average drift toward nega-

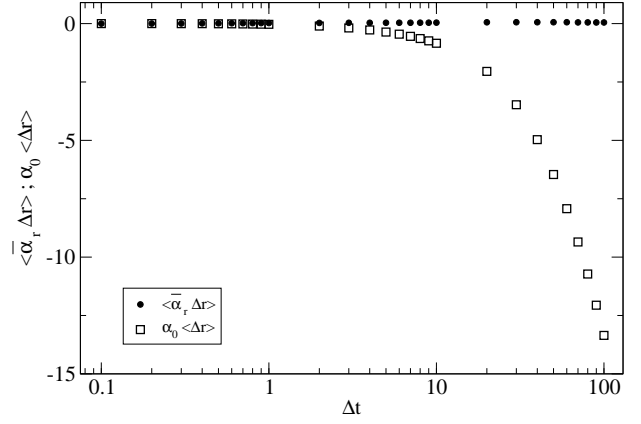


FIG. 4: Ensemble averages of  $\bar{\alpha}_r \Delta r$  (solid circles) and  $\alpha_0 \langle \Delta r \rangle$  (open squares) as a function of time  $\Delta t$ . Data computed from simulations of  $10^7$  trajectories of a particle traveling in a flat potential and a ramp friction function Eq. (41). The time step of the simulations:  $dt = 0.01$ .

tive values of  $r$ ; i.e., in the direction of the smaller friction coefficient.

When  $f \neq 0$ , we expect the force-drift relationship  $f \Delta t = \langle \bar{\alpha}_r \Delta r \rangle$  Eq. (23) to hold for large time scales  $\Delta t \gg \tau$ . To test the validity of this prediction, we performed two sets of simulations similar to those described in the previous paragraph, but now with non-vanishing forces  $f = 0.1$  and  $f = -0.1$ . These values of  $f$  have been chosen to make the deterministic force comparable to the spurious force  $f_s$  Eq. (19), and in order to examine both the situation where  $f$  and  $f_s$  are parallel to each other as well as the case where they point in opposite directions. The results of these simulations are summarized in Fig. 5, where we plot the ratio  $\langle \bar{\alpha}_r \Delta r \rangle / (f \Delta t)$  as a function of  $\Delta t$ . The figure demonstrates that the ratio indeed converges to unity at times much larger than the ballistic relaxation time  $\tau$ , which can be evaluated by  $m/\max(\alpha) = 0.2 < \tau < 2 = m/\min(\alpha)$ . The crossover into the large  $\Delta t$  regime occurs at somewhat smaller times when the deterministic and spurious forces are opposite to each other.

Finally, we arrive at the generalized fluctuation-dissipation relationship Eq. (28). To demonstrate the validity of this equation, we consider the same particle with normalized mass  $m = 1$  at constant temperature  $T$ , moving under the action of no force ( $f = 0$ ) in a medium with a parabolic friction function:  $\alpha(r) = 10 + 0.1r^2$ . At the initial time, an ensemble of  $10^7$  such (non-interacting) particles are placed at  $r^0 = 0$ , and with  $dt = 0.01$  we analyze their trajectories over time. The fact that the trajectories start from the minimum of a parabolic friction function ensures that, over time, the particles will arrive to further regions of the system with an ever-increasing  $\alpha(r)$ , which would prevent the friction coefficient from



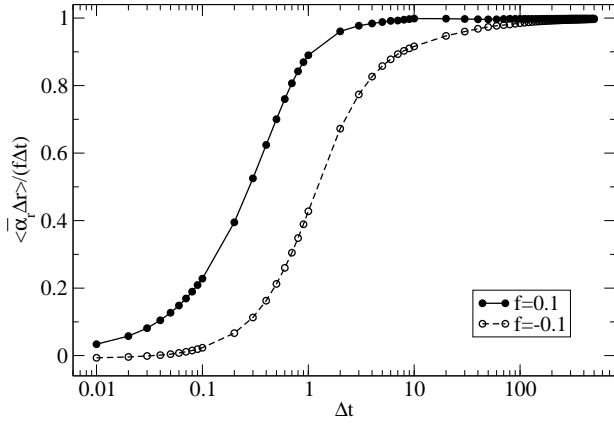


FIG. 5: Ratio between  $\langle \bar{\alpha}_r \Delta r \rangle$  and  $f \Delta t$  as a function of time  $\Delta t$  for  $f = 0.1$  (solid circles, solid line) and  $f = -0.1$  (open circles, dashed line). Data computed from simulations of  $10^7$  trajectories of a particle traveling in a linear potential  $-fr$  and a ramp friction function Eq. (41). The time step of the simulations:  $dt = 0.01$ .

“saturating”. We define the temperature  $T_1$ ,

$$k_B T_1 = \frac{\langle (\bar{\alpha}_r \Delta r)^2 \rangle}{2 \int_0^{\Delta t} \langle \alpha(t) \rangle dt}, \quad (42)$$

which, according to Eq. (28), is expected to converge to the thermodynamic temperature  $T$  at large times  $\Delta t \gg \tau$ . We also compare Eq. (28) with the standard form of the fluctuation-dissipation relationship [see Eqs. (1) and (6)], featuring the temperature  $T_2$

$$k_B T_2 = \frac{\alpha_0 \langle (\Delta r)^2 \rangle}{2 \Delta t}, \quad (43)$$

that would have converged to unity had the friction coefficient been constant  $\alpha(r) = \alpha(r^0) = \alpha_0 = 10$ . Our results, which are summarized in Fig. 6, demonstrate that  $T_1$  indeed converges to  $T$  - in full agreement with Eq. (28). In contrast, the value of  $T_2$  steadily decreases at large times, which exemplifies that  $\langle (\Delta r)^2 \rangle$  does not scale linearly with  $\Delta t$  as suggested by the conventional fluctuation-dissipation relationship. Notice that the large time behavior of  $T_2$  depends on the form of the function  $\alpha(r)$ . In the case studied here,  $\alpha(r)$  has a parabolic form and the friction coefficient increases from the initial value of  $\alpha_0$ . This would naturally lead to a decrease in  $T_2$ , which serves as a measure for the effective diffusion coefficient.

#### IV. CONCLUDING REMARKS

We conclude with the highlights of the study:

1. When a particle diffuses in a medium with spatially dependent friction coefficient, it exhibits a drift toward

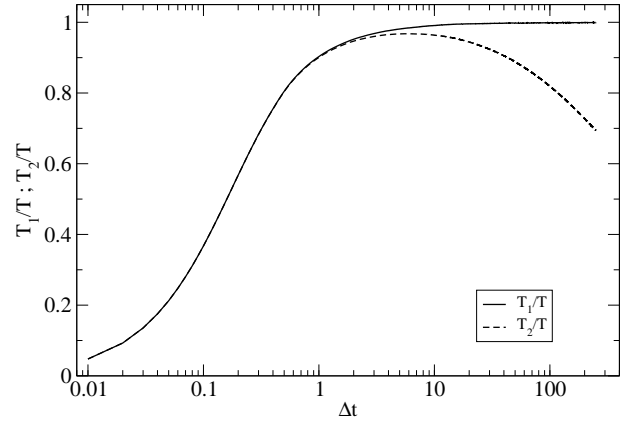


FIG. 6: Time dependence of the temperatures  $T_1$  [Eq. (42) - solid line] and  $T_2$  [Eq. (43) - dashed line] defined, respectively, from the generalized (for non-uniform  $\alpha$ ) and standard (for constant  $\alpha$ ) forms of the fluctuation-dissipation relationship. Data computed from simulations of  $10^7$  trajectories of a particle traveling in a flat potential and a parabolic friction function, where the initial position is at the minimum of the parabola. The time step of the simulations:  $dt = 0.01$ .

the low-friction end. The drift represents an inertial effect originating from the fact that when the particle travels toward a less viscous side, it suffers less dissipation and therefore travels longer distances. The drift counters the tendency of the particle to get trapped, due to slower diffusivity, in the more viscous parts of the system. The total amount of time spent by the particle in each part of the system is, obviously, independent of  $\alpha(r)$  and depends only on the potential energy (via the equilibrium distribution).

2. Since the drift results from an inertial effect, it needs to be studied within the framework of the full Langevin equation (2) and not by using its overdamped (massless) limit Eq. (5). While the former equation of motion is simply Newton’s second law with friction and noise, the latter equation is non-physical since it allows the velocity to diverge for an impulse of Gaussian white noise. This leads to the ambiguity known as Itô-Stratonovich dilemma of the interpretation of the stochastic integral. The dilemma is merely an artifact of the excessively simplified form Eq. (5). With the full Langevin equation, all the conventions of assigning a value for the friction coefficient would yield statistically similar trajectories in the limit when the time step  $dt \rightarrow 0$ . This leaves us with the “lighter version” of the dilemma concerning the convention with the best rate of convergence, which is an important computational issue.

3. We found the GJF integrator with the new inertial convention to be the best method for Langevin dynamics simulations. The method produces accurate thermodynamic behavior at large times for relatively large integration time steps, even in systems with very rough friction landscapes. The success of the method can be attributed in part to the merits of the GJF integrator (which produces correct thermodynamic response for constant  $\alpha$

[20]), and in part to the fact that the inertial convention uses two different friction coefficients:  $\bar{\alpha}_r$  and  $\bar{\alpha}_t$ . The former of the two friction coefficients governs the dissipative component of the integrated Langevin equation (10), and the latter sets the amplitude of the stochastic noise. While expression (11) for  $\bar{\alpha}_r$  is exact, expression (14) for  $\bar{\alpha}_t$  is not, but it ensures that the requirement of Eq. (15) for the noise is satisfied. This requirement is rooted in the way that the random collision forces are represented in the Langevin equation, where the friction describes the mean force impulse, and the noise accounts for the fluctuations around the mean force.

4. We derived three new equations to characterize the dynamics in media with non-uniform friction. Equations (16) and (28) describe the average and mean squared displacement in the absence of a deterministic force ( $f = 0$ ), while Eq. (23) gives the force-displacement relationship for  $f \neq 0$ . Notice that only the first equation

(16) holds for any time  $\Delta t$ , while the other two describe the asymptotic behavior for  $\Delta t \gg \tau$ . The equations involve the variable  $\bar{\alpha}_r \Delta r = \Delta A$  [where  $A(r)$  is the primitive function of  $\alpha_r(r)$ ], which emerges at the quantity that characterizes the statistical properties of the dynamics. The validity of the newly derived equations has been verified by computer simulations.

5. We demonstrated that our generalized form of the fluctuation-dissipation relationship (28) is consistent with Fick's second law (35), where the local diffusion coefficient  $D(r) = k_B T / \alpha(r)$ . We reemphasize that diffusion is a non-local process and, thus,  $D(r)$  bears physical meaning only within the context of a Fokker-Planck differential equation.

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- [1] A. Einstein, Ann. Phys. (Leipzig) **17**, 549 (1905).
  - [2] P. Langevin, C. R. Acad. Sci. (Paris) **146**, 530 (1908).
  - [3] G. Parisi, *Statistical Field Theory* (Addison Wesley, Menlo Park, 1988).
  - [4] K. Itô, Proc. Imp. Acad. Tokyo **20**, 519 (1944).
  - [5] R. L. Stratonovich, SIAM J. Contol. **4**, 362 (1966).
  - [6] J. L. Doob, Ann. Math **43**, 351 (1942).
  - [7] W. T. Coffey, Y. P. Kalmyfov, and J. T. Waldron, *The Langevin Equation: With Application in Physics, Chemistry and Electrical Engineering* (World Scientific, London, 1996).
  - [8] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
  - [9] P. Hänggi, Helv. Phys. Acta **51**, 183 (1978).
  - [10] H. Risken, *The Fokker-Planck Equation* (Springer-Verlag, Berlin, 1988).
  - [11] R. Mannella and P. V. E. McClintock, Fluct. Noise Lett. **11**, 1240010 (2012).
  - [12] A. W. C. Lau and T. C. Lubensky, Phys. Rev. E **76**, 011123 (2007).
  - [13] A. Bhattachary, preprint cont-mat:arXiv:1209.3654 (2012).
  - [14] A. G. Chersvy, A. V. Chechkin, and R. Metzler, N. J. Phys. **15**, 083039 (2013).
  - [15] O. Farago and N. Grønbech-Jensen, Phys. Rev. E **89**, 013301 (2014).
  - [16] D. T. Gillespie, *Markov Processes: An Introduction for Physical Scientists* (Academic, San Diego, 1992).
  - [17] P. Lançon, G. Batrouni, L. Lobry, and N. Ostrowsky, Europhys. Lett. **54**, 28 (2001).
  - [18] G. Volpe, L. Helden, T. Brettschneider, J. Wehr, and C. Bechinger, Phys. Rev. Lett. **104**, 170602 (2010).
  - [19] R. Mannella and P. V. E. McClintock, Phys. Rev. Lett. **107**, 078901 (2011).
  - [20] N. Grønbech-Jensen and O. Farago, Mol. Phys. **111**, 983 (2013).